Atomic Energy Control Board
P.O. Box 1046
Ottawa, Canada
K1P 5S9

Commission de contrôle de l'énergie atomique
C.P. 1046
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K1P 5S9

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AUTOMATED METHODS FOR THORIUM DETERMINATION IN LIQUIDS, SOLIDS AND AEROSOLS

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by

R. Robertson and J.E. Stuart
Becquerel Laboratories Inc.

RESEARCH REPORT

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AUTOMATED METHODS FOR THORIUM DETERMINATION IN LIQUIDS, SOLIDS AND AEROSOLS

Experimental work carried out and report prepared by R. Robertson and J.E. Stuart, Becquerel Laboratories Inc., under contract to the Atomic Energy Control Board.

ABSTRACT

Methodology for determining trace thorium levels in a variety of sample types for compliance purposes was developed. Thorium in filtered water samples is concentrated by ferric hydroxide co-precipitation. Aerosols on glass-fibre, cellulose ester or teflon filters are acid digested and thorium is concentrated by lanthanum fluoride co-precipitation. Chemical separation and measurement are then done on a Technicon AAII-C auto-analyzer via TTA-solvent extraction and colorimetry using the thorium-arsenazo III colour complex. Solid samples are acid digested and thorium is concentrated and separated using lanthanum fluoride co-precipitation followed by anion-exchange chromatography. Measurement is then carried out on the autoanalyzer by direct development of the thorium-arsenazo III colour complex. Chemical yields are determined through the addition of thorium-234 tracer with assay by gamma-ray spectrometry. The sensitivities of the methods for liquids, aerosols and solids are approximately 1 ug L^{-1}, 0.5 µg and 0.5 µg g^{-1} respectively. At thorium levels about ten times the detection limits, accuracy and reproducibility are typically ±10% for liquids and aerosols and ±15% for solid samples.

RÉSUMÉ

Le présent rapport fait état des méthodes mises au point pour déterminer les niveaux de traces de thorium dans une variété d'échantillons, afin de satisfaire aux exigences de conformité. Dans les échantillons d'eau filtrée, la concentration du thorium se fait par coprécipitation d'hydroxyde ferrique. Des acides digèrent les aérosols sur les filtres de fibre de verre, d'ester de cellulose ou "Teflon", et la concentration du thorium se fait par coprécipitation de fluorure de lanthane. La séparation et le dosage chimiques sont ensuite effectués sur un analyseur automatique Technicon AAII-C, par extraction au T.T.A. et au solvant, et par colorimétrie utilisant le complexe coloré de thorium-arsenazo III. Des acides digèrent les échantillons solides, tandis que la concentration et la séparation du thorium se font par coprécipitation de fluorure de lanthane, suivie du procédé chromatographique par échange anionique. Le dosage s'effectue ensuite sur l'analyseur automatique par développement direct du complexe coloré de thorium-arsenazo III. Le contenu chimique est déterminé grâce à l'ajout de thorium 234 comme traceur et essai par spectromètre de rayons gamma. Les méthodes utilisées pour les liquides, les aérosols et les solides présentent une sensibilité d'environ 1 µg L^{-1}, 0,5 µg et 0,5 µg g^{-1} respectivement. À des niveaux de thorium d'environ dix fois supérieurs aux limites de détection, l'exactitude et la reproductibilité sont normalement de ±10% pour les liquides et les aérosols et de ±15% pour les échantillons solides.

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PREFACE

Procedures and equipment have been developed in response to AECB's requirement for thorium analysis capability in connection with anticipated regulations and compliance testing. The goal of the methodology has been to attain as high a degree of automation as possible within the time and financial constraints of the project while retaining broad scope in sample types tractable. Sample preparation chemistry has been minimized in fast batch processes and emphasis placed on maximal utilization of a Technicon AAII-C autoanalyzer.

The developed procedures are capable of handling a wide variety of essentially inorganic samples of the types ordinarily encountered in occupational health and environmental monitoring. Laboratory testing has been carried out upon the following: fresh water samples of drinking or near-drinking quality; powdered solid samples including uranium ore, uranium tailings, soils, lake sediment and fly-ash; simulated aerosols on filters of the sort prevailing in uranium mining operations. All of these are successfully handled with sensitivity, accuracy and reproducibility as indicated in Appendix A. The procedures are not designed to handle organic materials or biological samples such as blood, urine or bone. Nor has the method been tested upon samples from industrial processes containing extraordinarily high levels of major interfering elements such as zirconium, the rare-earths and uranium.

The body of this report is descriptive in nature and outlines the methods and the reasoning leading to their selection. Stepwise operating procedures are given as appendices. Recommendations for further work to improve the methodology are given in Section C.

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AUTOMATED METHODS FOR THORIUM DETERMINATION
IN LIQUIDS, SOLIDS AND AEROSOLS

A. SAMPLE PREPARATION

1. Introduction

The sample preparation procedures consist of chemical and physical steps to concentrate and separate thorium into small volumes of solution suitable for analysis finishing via a Technicon AAII-C autoanalyzer. For water samples and aerosols, which constitute the great majority of the samples to be processed, concentration is achieved by co-precipitation followed by dissolution of the precipitate in a solution of suitable volume and pH for immediate presentation to the autoanalyzer. The burden of chemical separation of thorium from interferants lies, in these cases, upon the autoanalyzer methodology which includes a solvent extraction step.

For solid samples, it has been found necessary to include an anion-exchange step in the sample preparation chemistry in order to sufficiently separate thorium from interferants. In this case, the autoanalyzer is used simply as an automated colorimeter for thorium quantitation. With minor further development work, it is probable that the ion-exchange step could be substituted by solvent extraction on the autoanalyzer, bringing the overall methodology for solid samples in line with that for water samples and aerosols. As well as shortening the procedure for solid samples, the need to switch between alternate operating modes for the autoanalyzer would be eliminated.

The sample preparation chemistries are based on information and classical procedures in The Radiochemistry of Thorium.[1]

2. Preparation of Water Samples

Samples are collected in polyethylene bottles. Where significant quantities of suspended solids are present, the samples are vacuum filtered over a glass-fibre filter disc as soon as possible after collection. The samples are then acidified to 1% in concentrated nitric acid and stored in polyethylene bottles. Aliquots of 500 ml are transferred to 1000 ml clear plastic beakers (polymethylpentene, PMP) to begin the analysis. Thorium-234 tracer and 5 mg iron(III) carrier are added.

Ammonium hydroxide solution is added and thorium is concentrated from solution via ferric hydroxide co-precipitation. Lanthanum hydroxide was avoided as co-precipitant because the rare-earth elements are potential interferants through the formation of coloured complexes with arsenazo-III. Co-precipitation was chosen over ion-exchange concentration on grounds of speed and simplicity.

After allowing about 1 hour for the hydroxide precipitate to agglomerate and settle, the solution is vacuum filtered through a glass-fibre filter disc under a glass wool plug. The glass wool plug prevents filter

blockage and allows rapid filtration. Use of the PMP beakers for the precipitation allows quantitative transfer of the solution and precipitate to the filter assembly without washing. The collected precipitate is washed on the filter with a few millilitres of water to remove excess alkali.

The precipitate is dissolved and then washed through the filter with vacuum assistance using about 9 ml of 5% hydroxylamine hydrochloride solution adjusted to pH 1 with hydrochloric acid. This solution solubilises the precipitate through reduction of the iron (III) to iron (II). The collected solution is transferred to a volumetric flask and adjusted to 10 ml with the same solution. The sample solution will have pH in the range 1.2-1.8 which is optimum for the autoanalyzer solvent extraction step to follow. Having the carrier iron in the (II) state is advantageous since in this form it is essentially non-extractable.

At this stage, the thorium-234 content of the solution is assayed in the 10 ml volumetric flask by gamma-counting to determine chemical yield which typically will be 85-95%. A 2-3 ml aliquot of the solution is then presented to the autoanalyzer for solvent extraction separation of thorium and colorometric quantitation against similar solution standards of known thorium concentration.

3. Preparation of Aerosol Samples

Aerosol samples typically consist of < 2 mg aerosol material on 25 mm or 47 mm filter substrates of glass-fibre, cellulose ester or teflon. Each is placed in a 100 ml PMP beaker. Thorium-234 tracer solution and 5 ml each of half-concentrated nitric, hydrochloric and hydrofluoric acids are added. The beakers are then covered with plastic watch-glasses and placed on a hot-plate with surface temperature 125°C for one hour. During this digestion, filter substrates other than teflon normally dissolve.

The beaker covers are then removed and 25 ml 5% boric acid is added to complex fluoride ion. This solubilises any otherwise insoluble fluorides, especially those of the rare-earths and thorium, which may have formed. Complexation of the fluoride ion may force silica out of solution as a gelatinous precipitate which entrains any insoluble organic materials. About one hour after addition of the boric acid, the beakers are removed from the hot-plate.

The supernatant solution containing the thorium is recovered by vacuum filtration of the solutions through a glass-fibre filter disc. The precipitate is washed on the filter with 5 ml distilled water. The filtrate and washings are collected in a 50 ml polycarbonate centrifuge tube. Lanthanum carrier (5 mg) and 3 ml concentrated hydrofluoric acid are then added to concentrate thorium from solution via lanthanum fluoride co-precipitation. (See Section C, item 4 for comments on the use of lanthanum as carrier).

A waiting period of about 1 hour on a water-bath at approximately 80°C or overnight at room temperature is then allowed for complete precipitation and agglomeration. The tubes are then centrifuged for 5 minutes at 1500 rpm prior to decantation of the supernatant to waste. The precipitate is then washed with 10 ml water and the centrifugation step repeated. The wash solution is decanted to waste and 5 ml 10% aluminum nitrate solution adjusted to pH 1.5 is added to the precipitate in the tube. Using a disposable polyethylene pasteur pipet, the solution and precipitate are stirred and the tube is then placed on a hot-water bath for about 15 minutes to effect dissolution of the precipitate. The solution is then made up to 10 ml in a volumetric flask with the same aluminum nitrate solution and the chemical yield, which will typically be 80-90%, determined by gamma-counting of the thorium-234 tracer. A 2-3 ml aliquot of the solution, which will have pH 1.2-1.8, is then presented to the autoanalyzer for solvent extraction separation of thorium and colorometric assay against similar solution standards of known thorium concentration.

It is noted at this point, that substantial difficulties were encountered when attempts were made to develop a fast batch filtration method for handling the lanthanum fluoride precipitate. The main problems were slow filtration due to filter blockage and difficult recovery of the precipitate from the filter.

4. Preparation of Solid Samples

Powdered solid samples ($\leq$ 100 mesh, $\leq$ 0.5 g) are weighed into 100 ml FMP beakers. Sample digestion and co-precipitation and recovery of the thorium with lanthanum fluoride is then essentially identical to the procedure described for aerosols in item 3 above. The single difference is the use of a glass-wool plug over the glass-fibre filter in the filtration step after the acid digestion. This speeds filtration by holding back from the filter the normally formed voluminous and gelatinous silica precipitate.

After dissolution of the lanthanum/thorium fluoride precipitate with 5 ml 10% aluminum nitrate, 5 ml concentrated nitric acid is added to the solution. The solution is then passed over a 0.7 x 5 cm anion exchange column conditioned in half-concentrated nitric acid. The column flow-rate is not critical but should be in the range 0.5-1.0 ml per minute. Thorium is retained on the column as a negatively charged nitrate complex. The column is washed with half-concentrated nitric acid which removes aluminum, lanthanum and practically all potential interferants. An exception is uranium which is weakly adsorbed but which in normal cases would have been sufficiently separated in the previous fluoride co-precipitation step.

Thorium is eluted from the column directly into a 10 ml volumetric flask using 10 ml 3% sulphuric acid solution. The complexing action of the sulphate ion is useful in removing thorium from the column in an acceptably small volume while not being strong enough to unduly interfere later in the thorium-arsenazo III colour development step on the autoanalyzer.

The column eluates are gamma- counted for thorium-234 to determine chemical yields which are typically 70-90%. Aliquots of 2-3 ml are presented to the autoanalyzer for thorium quantitation against similar solution standards of known thorium concentration.

5. Thorium-234 Tracer Preparation

Thorium-234 (half-life 24.1 days) is generated through α-decay of ~30 g uranium-238 held as the chloride complex on an anion exchange column. The column bed volume is about 250 ml with dimensions 2.5 x 50 cm. The resin is Bio-Rad AG1-X8 100-200 mesh chloride form conditioned in 9 N HCl.

An amount of uranium (VI) oxide equivalent to ~30 g uranium-238 is dissolved in 1.2 L 9 N hydrochloric acid. The solution is filtered through a glass wool plug to remove any insoluble material and then passed through the column. The uranium is retained on the top 30 cm of the column. Any thorium in the loading solution is washed from the column using 1 L 9 N hydrochloric acid. The column is then ready for use.

The column generates in 1 day sufficient thorium-234 for 12 sample analyses. A generation period of 1 month yields enough tracer for 200 samples. It is recommended that the column be eluted at least once per month whether needed or not in order to avoid excessive concentration of dissolved resin in the free-volume solution, to maintain the column in proper condition and to avoid the build-up of weighable quantities of thorium isotopes. Discard the column after 6 months.

To prepare tracer, thorium isotopes are eluted from the column with 150 ml 9 N hydrochloric acid. This solution is evaporated to about 10 ml and then an equal volume of 9 N hydrochloric acid is added. This solution is passed over a 0.7 x 5 cm bed of the same resin used to make the generator column. This removes traces of uranium. The effluent solution from this second column is then evaporated to dryness. A residue is normally evident which is mainly ion-exchange resin dissolved from the generator column. The residue is dissolved in 10 ml 8 N nitric acid and the solution is passed over a 0.7 x 5 cm bed of the same resin conditioned in 8 N nitric acid. The column adsorbs thorium as a nitrate complex whereas impurities such as dissolved resin and traces of other elements pass through. The column is then washed with 2 x 5 ml 8 N nitric acid. The thorium-234 tracer is eluted with 20 ml 1 N hydrochloric acid and diluted as required.

B. AUTOANALYZER METHODOLOGY

1. Introduction

The Technicon Autoanalyzer AAII-C is a continuous flow system designed to handle the analysis of large numbers of liquid samples. The modular nature of the system allows considerable flexibility in its chemistry and detection functions.

The autoanalyzer procedures developed in this work are largely modifications of the manual methods for thorium currently in use at the AECB, Ottawa laboratory (See Appendix F). Chemical reactions, solvent extractions and colour development are now performed automatically, precisely and on a small scale by mixing coils and phase separators as described below. The flow diagrams overleaf give a diagramatic representation of the chemical processes used.

For water and aerosol samples prepared as described in Section A, a solvent extraction step is the key element of the autoanalyzer process. In the pH 1-2 range which is used for the extraction, thorium is fully extracted by formation of the thorium-TTA complex. Interfering elements such as the rare-earths only extract at pH > 2 and are therefore separated. The thorium is then fully back-extracted at pH < 0, whereas other major interfering elements such as zirconium, hafnium and uranium remain in the solvent phase.

For prepared solid samples, the autoanalyzer is used simply as an automatic colorimeter.

2. Analysis of Water Samples and Aerosols

Aliquots of 2-3 ml of samples and standards in the same chemical composition are placed in the autoanalyzer sample tray and are sequentially aspirated, one every 2 minutes. As the sample enters the system it is air segmented every 2 seconds before it is mixed with reagents. The air bubbles break the sample into several smaller segments whose integrity is maintained by the wiping action of the bubbles as they pass through the tubing. Thus the samples are well separated from each other and sample carry-over is minimized. Carry-over is further minimized by between sample washing with 2 $\underline{N}$ HNO_3 (from wash reservoir). This effectively dissolves any thorium which may have been adsorbed onto the tubing walls from the pH 1.5 samples for the solvent extraction chemistry. Thorium is not appreciably solvent extracted from 2 $\underline{N}$ HNO_3 so this "washed off" thorium does not appear.

The autoanalyzer is set up as in the flow diagram, Figure 1 following general techniques for connecting components and tubing as outlined in the Technicon Users Manual. The system is "primed" for 10 minutes by pumping water through the lines which will carry aqueous reagents, and kerosene through the line which will be used for the thenoyltrifluoroacetone in kerosene reagent. The analyser is then switched over to the pump reagents in all lines (sample probe remains in the sample reservoir containing 2 $\underline{N}$ HNO_3).

Figure 1: Flow Diagram for Thorium Analysis on Technicon AA II-C - Solvent Extraction Method

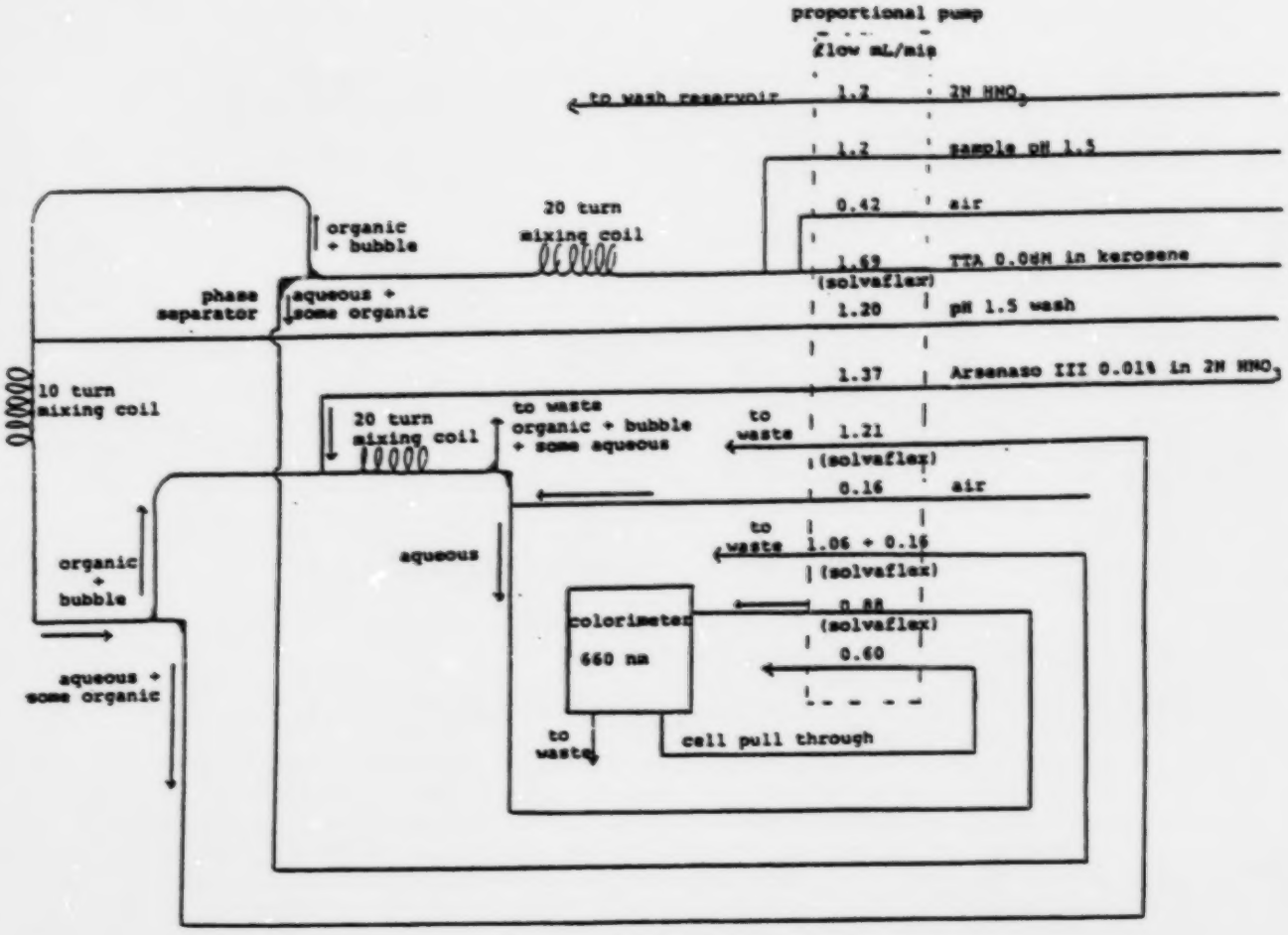
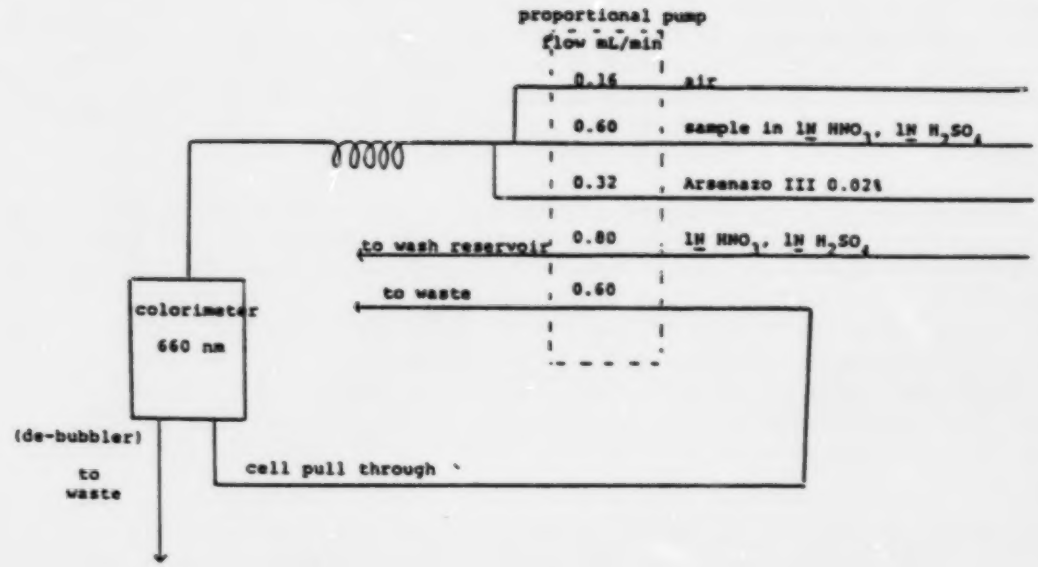


Figure 2: Flow Diagram for Thorium Analysis on Technicon AA II-C "Straight" Chemistry



After a steady baseline has been maintained for at least 10 minutes, the samples and standards can be run. Aliquots of 2-3 ml of standards and samples are transferred into individual sample cups and placed in the sample tray. Typically, two calibrating standards of 1.0 ug ml^{-1} Th are run to set the full scale readout followed by a series of standards covering the 0.1 to 1.0 ug ml^{-1} Th range, then the samples and finally a 1.0 ug ml^{-1} Th standard to check for changes in calibration.

As the sample enters the autoanalyzer it is air segmented then mixed with 0.08 M thenoyltrifluoroacetone (TTA) in kerosene. The mixture passes into a 20 turn mixing coil where the extraction of the thorium (IV) into the organic phase takes place. Several steps are taken to maximize the aqueous-organic interface area. A small teflon insert on the upper half of the straight glass segment of the mixing coil repels the aqueous phase and results in the organic phase riding on top of the aqueous phase. The length of this insert and the flow rates have been adjusted so that each air bubble separated segment in the mixing coil is made up of several organic-aqueous segments. By the time the mixture has passed through the 20 turn mixing coil, the two phases have migrated so that in most cases each segment is made up of a single organic phase followed by the aqueous phase. After this point, further mixing does not effect much additional extraction.

The mixture proceeds to a phase separator where the aqueous phase plus a small amount of the organic phase is pulled off to waste. The two phases are separated by virtue of their different densities. Clean separation is aided by a small teflon insert which "guides" the organic phase. The organic phase plus the segmenting bubble is then mixed with a "wash" solution (2% saturated ammonium acetate pH adjusted to 1.5) and the phases separated with the wash solution going to waste. The organic phase is then mixed with 2 N HNO_3 containing 0.01% arsenazo III colour reagent in a 20 turn mixing coil to back extract the thorium into the aqueous phase.

In a final phase separation, the aqueous phase is retained and then pumped into the colorimeter where the absorbance at 660 nm is measured. The time between the start of sample aspiration and the appearance of the peak on the chart recorder is approximately 8 minutes.

3. Analysis of Solid Samples

The autoanalyzer is set up as in the flow diagram, Figure 2. The system is "primed" for 10 minutes by pumping distilled water through all reagent lines. Reagents are then pumped through their designated lines until a steady baseline has been maintained for about 10 minutes.

Aliquots of 1.5 - 2 ml of samples and standards are placed in sample cups in the sample tray as for the analysis of water and aerosol samples. Standards are in the range of 0.1 to 1.0 ug m^{-1} thorium in a solution approximately 1N in both nitric and sulphuric acids. The samples enter the autoanalyzer and are air bubble segmented then mixed with 0.02% arsenazo-III in a ten turn mixing coil. The absorbance of the thorium-arsenazo III colour complex is then measured at 660 nm. The time between the start of sample aspiration and the appearance of the peak on the chart recorder is about 5 minutes.

C. GENERAL REMARKS ON THE METHODOLOGY

1. Sample Preparation Equipment

The general aim of this project was to develop methodology which would allow the required analyses to be simply performed at acceptably high through-put rate with minimum labour input. In response to this, equipment has been assembled which allows the pre-autoanalyzer chemistry to be carried out in parallel on batches of 12 samples. Equipment which is readily available commercially has been selected wherever possible. Following good practice for trace inorganic analysis, plastic materials have been chosen throughout wherever possible, especially for items in contact with samples. Such items have the additional advantage of allowing essentially quantitative decantation of solutions and precipitates without washing.

The key item of the pre-chemistry equipment is a commerically supplied vacuum filtration manifold. With small modification, this allows for rapid filtrations and easy recovery of both precipitates and filtrates. Its plastic construction is compatible with all of the contemplated chemistry, including that involving hydrofluoric acid. This item is illustrated in Figure 3. Its internal fittings for filtrate collection are shown in Figure 4. Figures 5 and 6 show a plexiglass tray and a plexiglass column holder which facilitate solid sample acid digestions and column chromatography respectively. These items were designed and built for this project. The Technicon AAII-C autoanalyzer is not described here. The reader is referred to the operator's manual.

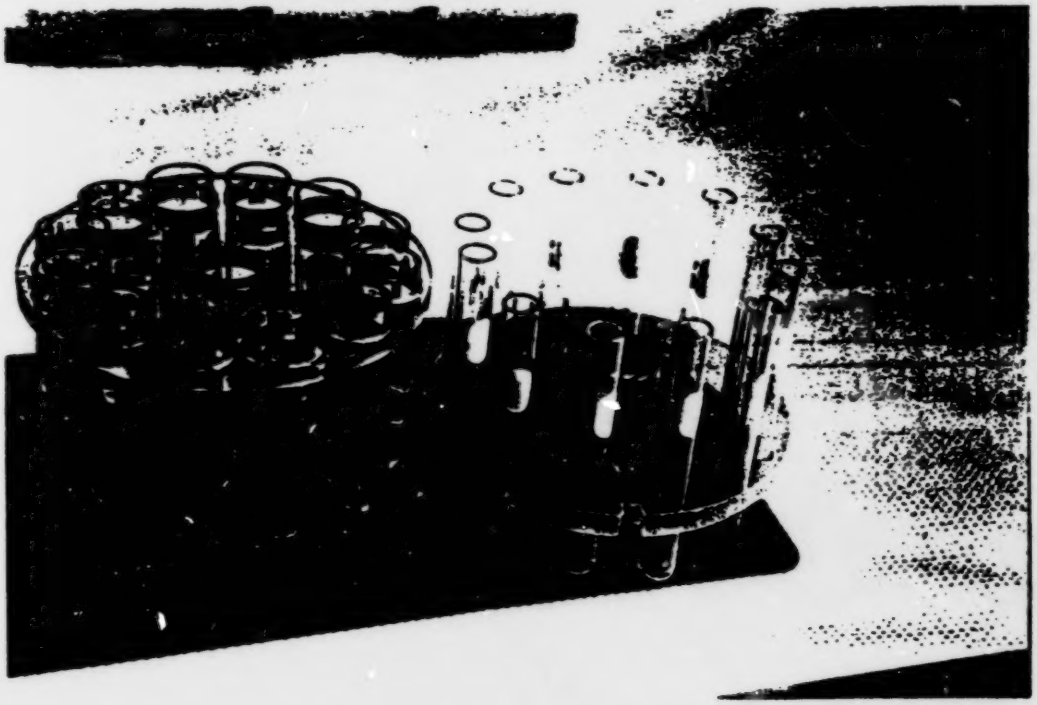
2. Autoanalyzer Procedures

In modifying the manual method currently in use at AECB, kerosene was used in place of benzene as the solvent for the complexing thenoyltrifluouroacetone (TTA). The solubility of TTA is not as high in kerosene as it is benzene but is sufficient for the low levels of thorium expected. Benzene was avoided because of its inherently nasty characteristics, i.e., carcinogenic, low boiling point, low flash point and special tubing requirements for the autoanalyzer. Also since 2 N HNO_3 was experimentally proven to be as good as 2 N HCl for the formation of the thorium-arsenazo III complex, the back extraction and colour development steps could be combined and the steps required to obtain thorium in a nitrate free solution where eliminated.

One of the most important requirements of the autoanalyzer is that the samples and standards be as nearly identical as possible in chemical nature since good accuracy depends on reactions proceeding under identical conditions. The preparation of the solid samples gives a final solution of thorium approximately 1 N in both nitric and sulphuric acids. Sulphate ion forms a complex with thorium which results in a response of only 70% of that for the formation of the complex in 2 N nitric acid. Therefore the standards for this chemistry must also be approximately 1 N in both nitric and sulphuric acids. A similar argument applies to the preparation of standards for the water and aerosol samples.

Figure 3: Millipore vacuum filter manifold and pump.

Figure 4: Internal filtrate collection fittings for above manifold.



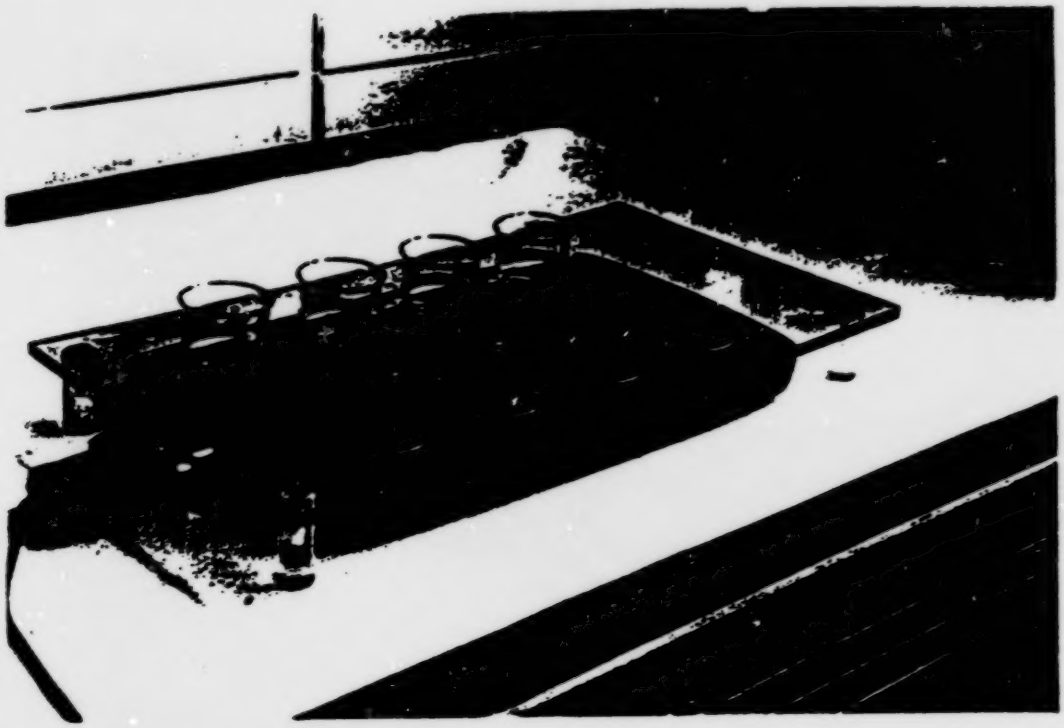
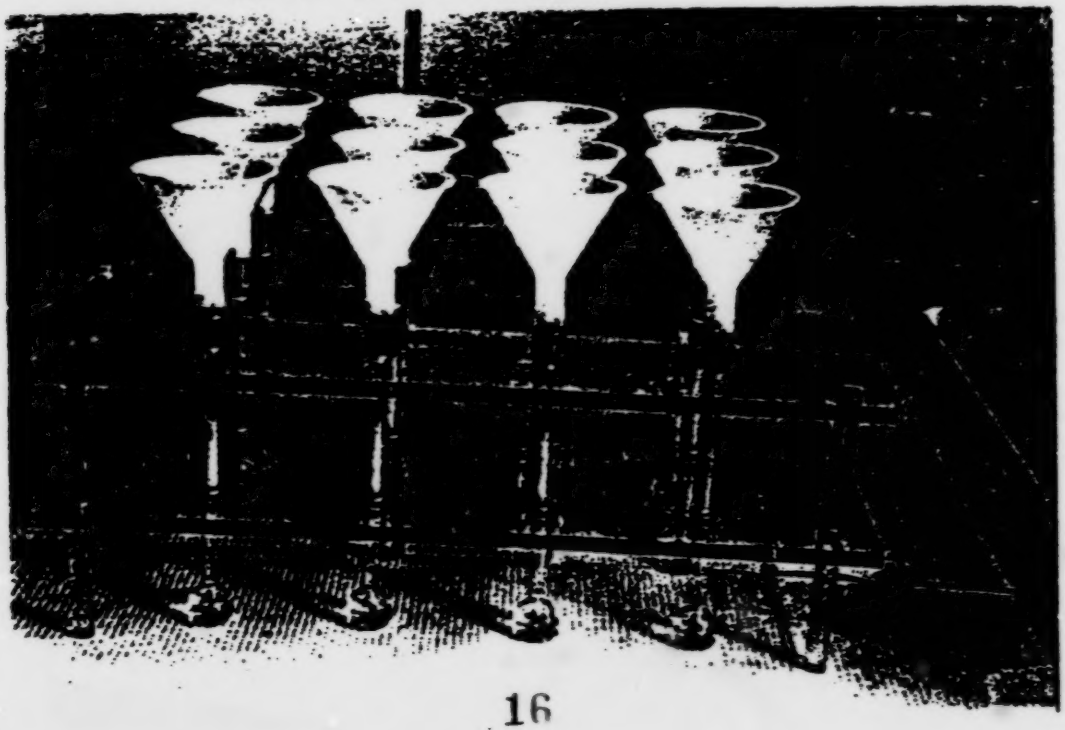


Figure 5: Beaker tray and hotplate used for aerosol and solid sample digestions.

Figure 6: Ion-exchange column rack with columns in thorium elution stage.



3. Sample Through-Put

A batch of 12 water samples, taken from storage already filtered and acidified, may be processed up to the autoanalyzer stage in about two hours. Chemical yield detemination would require approximately one hour further, depending upon the quantity of thorium-234 added and the counting equipment used for its assay. Processing of several standards and the 12 samples through the autoanalyzer would take about 1.5 hours, given that the machine is set up and ready to run. Data reduction and results documentation would require about one hour. Allowing about one hour for miscellaneous tasks, such as reagent preparation and machine set-up, leads to a total elapsed time of six to seven hours for the processing of 12 water samples. The labour input would be about five person-hours, less than 0.5 person-hours per sample.

A batch of 12 solid or aerosol samples may be processed up to the autoanalyzer stage in about seven hours. Allowing one hour each for chemical yield determinations, autoanalyzer process, data reduction and miscellaneous tasks results in a total elapsed time of 11 hours. The total labour input would be about eight person-hours, or about 0.75 person-hours per sample.

4. Recommendations for Further Work

Although satisfactory methods have been developed, there is room for worthwhile improvements to be made in these procedures. This is normal for work of a development nature carried out under time and financial limitations.

The most obvious and desirable improvement to be made is to bring the procedure for solid samples more in line with those for water and aerosol samples. This would mean eliminating the anion-exchange step in the solid sample method and substituting it with a solvent extraction step on the autoanalyzer. This was almost achieved during the current contract, but the results were not considered reliable enough. The problem would be to identify and eliminate the interferences responsible for the inconsistent results. The advantages of the change would be to speed up the analyses and to avoid switching between operating modes for the autoanalyzer.

A second improvement worth investigating would be to treat the digested aerosol samples similarly to water samples. This would mean concentrating thorium from alkaline solution using ferric hydroxide as carrier, rather than from acid solution using lanthanum fluoride. The advantage of this would be to eliminate from the chemistry a relatively large mass of a major potential interferant. This change would be a precaution only and would not be expected to improve speed or quality since the autoanalyzer solvent extraction normally gives excellent separation from lanthanum.

In this regard, it is noted that it would also be desirable to eliminate lanthanum fluoride co-precipitation as a concentration step for solid sample treatment. In this case any co-precipitation must be carried out from acid solution to avoid precipitation of the large quantities of

aluminum and iron hydroxide which would form in basic solution in the treatment of most solid samples. There appears to be no good alternative to lanthanum fluoride co-precipitation and therefore it may not be practical to eliminate this step. It may be possible, however, to selectively complex lanthanum after the fluoride co-precipitation step and to allow a lanthanum-free ferric hydroxide co-precipitation to be carried out. This possibility and other means of eliminating rare-earth carriers are worth looking into.

The overall aim of the improvements would be to further gain in efficiency and reliability of operation by eliminating time consuming steps in the sample preparation chemistry, by eliminating the addition of potentially interfering carriers and by standardizing the autoanalyzer procedures and comparator solutions.

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APPENDIX A

RESULTS, ACCURACY, PRECISION AND SENSITIVITY

Water Samples

The results for 16 water samples are given in Table A1. Some of these are real samples and some are spiked samples to check accuracy and precision. The chemical yield is calculated from the thorium-234 tracer recovery. The found values for thorium are corrected for this chemical yield.

There is insufficient data to make a detailed statistical evaluation. Inspection of the data indicates that accuracy and precision of the method are within $\pm$10% and that the detection limit is about 1 ug L^{-1}.

Aerosol Samples

The results for 10 simulated aerosol samples and 2 blanks are given in Table A2. The aerosol material itself was simulated by approximately 2 mg of a uranium failings sample UTS-3 (CANMET) which has thorium content of 10.0 ug g^{-1}. This material was simply added to a filter in a beaker prior to the digestion step.

Inspection of the data indicates that the accuracy and precision of the method are within $\pm$10% and that the detection limit is about 0.5 ug.

Solid Samples

The results for 12 solid reference materials and 2 blanks are given in Table A3. Inspection of the data indicates that the accuracy and precision of the method are within $\pm$15% and that the detection limit is about 0.5 ug g^{-1}.

TABLE A1: Results for Water Samples

All samples are 500 ml except where noted

Sample Description	Chemical Yield *	Th Added	Th Found
1. Distilled Water (blank)	93%	None	<0.5 ppb
2. Distilled Water	94%	10.3 ppb	10 ppb
3. Tap Water (Ottawa)	89%	None	<0.6 ppb
4. Tap Water (Ottawa)	96%	2.1 ppb	2.2 ppb
5. Tap Water (Ottawa)	90%	14.2 ppb	15 ppb
6. Tap Water (Ottawa)	97%	20.0 ppb	19 ppb
7. Tap Water (Mississauga)	81%	10.0 ppb	8.6 ppb
8. Tap Water (Mississauga)	92%	10.0 ppb	9.8 ppb
9. Tap Water (Mississauga)	94%	10.0 ppb	8.9 ppb
10. Tap Water (Mississauga)	84%	10.0 ppb	9.5 ppb
11. Credit River water (Mississauga)	85%	None	<1 ppb
12. Spring water (Mississauga)	91%	None	<1 ppb
13. Melted snow (Mississauga)	93%	None	<1 ppb
14. AECB sample 2103 (380 ml)	93%	None	1.3 ppb
15. AECB sample 3104 (380 ml)	95%	None	<0.5 ppb
16. AECB sample 2109 (1 ml)	93%	None	2370 ppb

* The counting statistical error (1 sigma) for Th-234 tracer recoveries for these analyses was <2%.

TABLE A2: Results for Simulated Aerosol Samples

All aerosols simulated by ~2 mg UTS-3(CANMET) uranium tailings

	Substrate Description*	Chemical Yield **	Th Added	Th Found
1.	Blank	81%	None	<0.3 ug
2.	Blank	90%	None	<0.3 ug
3.	GN-6, 25 mm	85%	3.9 ug	4.0 ug
4.	GN-6, 25 mm	59%	2.1 ug	1.9 ug
5.	Glass fibre, 25 mm	92%	5.0 ug	4.6 ug
6.	Glass fibre, 25 mm	98%	5.0 ug	4.8 ug
7.	Glass fibre, 25 mm	92%	5.0 ug	4.8 ug
8.	Glass fibre, 25 mm	93%	5.0 ug	4.9 ug
9.	Glass fibre, 25 mm	91%	5.0 ug	4.9 ug
10.	Teflon, 25 mm	90%	5.0 ug	4.7 ug
11.	Teflon, 25 mm	83%	5.0 ug	5.0 ug
12.	Teflon, 25 mm	74%	5.0 ug	5.3 ug

* GN-6 is a cellulose ester filter by Gelman. The glass-fibre filters were Whatman 934-AH. The teflon filters were Mitex 10 micron by Millipore.

** The counting statistical error (1 sigma) for Th-234 tracer recoveries for these analyses was <3%.

TABLE A3: Results for Solid Samples

All samples were approximately 0.5 grams.

	Substrate Description*	Chemical Yield *	Th Content**	Th Found
1.	Blank	81%	—	<0.5 ppm
2.	Blank	84%	—	<0.5 ppm
3.	Uranium Tailings UTS-3 (CANMET)	88%	(10.0 ppm)	9.4 ppm
4.	Uranium Tailings UTS-3 (CANMET)	91%	(10.0 ppm)	9.1 ppm
5.	Uranium Tailings UTS-3 (CANMET)	91%	(10.0 ppm)	9.4 ppm
6.	Uranium Tailings UTS-3 (CANMET)	84%	(10.0 ppm)	9.0 ppm
7.	Uranium Tailings UTS-3 (CANMET)	89%	(10.0 ppm)	8.8 ppm
8.	Uranium Tailings UTS-4 (CANMET)	75%	(15.4 ppm)	15 ppm
9.	Lake sediment SL-1 (IAEA)	94%	14 ppm	13 ppm
10.	Soil SOIL-5 (IAEA)	94%	11.3 ppm	12 ppm
11.	Soil SO-1 (CANMET)	88%	(12 ppm)	10 ppm
12.	Soil SO-2 (CANMET)	87%	(3.7 ppm)	4.5 ppm
13.	Uranium ore BL-3 (CANMET)	90%	15 ppm	15 ppm
14.	Fly-ash 1633a (NBS)	84%	24.7 ppm	28 ppm

* The counting statistical error (1 sigma) for Th-234 tracer recoveries for these analyses was <3%.

** Non-bracketted values are certified values; bracketted values are information values only.

APPENDIX B

STEPWISE PROCEDURES FOR SAMPLE PREPARATION

Water Samples

1. Transfer 500 ml of sample to a clean 1000 ml polymethylpentene (PMP) beaker.

2. Add 1 ml thorium-234 tracer solution.

3. Add 1 ml iron carrier solution.

4. Thoroughly stir the solution, then add 15 ml 7.6 N NH_4OH solution while continuing to stir.

5. Cover the beaker and wait at least 1 hour.

6. Set up the Millipore vacuum filter manifold and pump with 25 mm glass-fibre filters under glass-wool plugs and 50 ml extension barrels in place. The manifold reservoir should be empty and any filter ports not to be used should be closed with neoprene stoppers.

7. Filter the solutions, pausing to drain the filter manifold (volume approximately 2.5 L) as required. Discard the solutions to waste.

8. Wash each ferric hydroxide precipitate on the filter under slight vacuum with 3-5 ml water.

9. Switch off the pump, drain the manifold to waste and, keeping the two top plates of the manifold firmly together, remove them from the manifold and place on a clean surface.

10. Wipe out the interior of the manifold and insert the test tube holder with the appropriate number of 16 x 125 mm test tubes in place.

11. Re-assemble the manifold and connect to the pump but do not switch on the pump.

12. Add 5 ml 5% hydroxylamine hydrochloride solution pH 1 to each precipitate and thoroughly stir using a disposable polyethylene pasteur pipet.

13. Wait 15 minutes, then apply slight vacuum to the filters and pull the solution through to the collecting test tubes.

14. Switch off the pump and then add a further 4 ml of the 5% hydroxylamine solution to the filters and stir.

15. Pull the solutions through the filters to the collection tubes and then switch off the pump.

16. Disassemble the filter manifold and transfer the solutions to 10 ml volumetric flasks. Make up to the mark with the same 5% hydroxylamine pH 1 solution.

17. Gamma-count the solutions in the volumetric flasks to determine chemical yield. Integrate the spectra between 60 and 95 keV. Subtract background similarly counted and integrated. Compare sample solution counts with 1 ml of tracer taken directly as a comparator and made up to 10 ml in a volumetric flask.

18. Transfer the solutions to plastic bottles pending the autoanalyzer finishing process. Check that the pH's are in the range 1.2-1.8. Adjust if necessary using a drop or two of 7.6 N NH_4OH or 6 N HCl.

Aerosol Samples

1. Place each aerosol sample and filter in a clean 100 ml polymethylpentene (PMP) beaker.

2. Add 1 ml thorium-234 tracer solution.

3. Add 5 ml each of 8 N HNO_3, 6 N H Cl and 14 N HF.

4. Cover beakers with close fitting plastic watch-glasses (do not use Speedy-Vap ribbed covers) and place on hotplate with surface temperature about 125°C for 1-2 hours.

5. Remove beaker covers but leave beakers on the hotplate. Add 25 ml 5% boric acid to each sample. Leave beakers uncovered on hot-plate for 1 hour further.

6. Set up Millipore vacuum filtration manifold with glass-fibre filter discs and 50 ml polycarbonate centrifuge tube receivers in place as appropriate. Close with neoprene stoppers any ports which are not used. It is not necessary to use the extension barrels for this filtration.

7. Pass the sample solutions through the filters and wash the PMP beakers and the filters each with 5 ml water. Note that each filtrate and wash combined should not exceed 40 ml.

8. Add 1 ml lanthanum carrier solution (5 mg La) to each centrifuge tube and mix thoroughly using a plastic stir-stick.

9. Add 3 ml 14 N HF and again stir. Remove the stir-stick.

10. Place tubes on water-bath at about 80°C for at least 1 hour or leave overnight at room temperature.

11. Spin tubes at 1500 rpm for 5 minutes then decant supernatant solution to waste.

12. Wash precipitate with 10 ml water. Repeat the centrifugation step and decant the wash solution to waste.

13. Add 5 ml 10% $Al(NO_3)_3$ pH 1.5 solution to the precipitate in the tube. Stir the tube contents using a polyethylene pasteur pipet and place the tube on a water-bath at about 80°C for at least 15 minutes to effect dissolution of the precipitate.

14. Make the solution to 10 ml with 10% $Al(NO_3)_3$ pH 1.5 solution in a volumetric flask.

15. Gamma-count the solutions in the volumetric flask to determine chemical yield. Integrate the spectra between 60 and 95 keV. Subtract background similarly counted and integrated. Compare sample solution counts with 1 ml tracer solution taken directly as a comparator and made up to 10 ml.

16. Transfer the solutions to plastic bottles pending the autoanalyzer finishing process. Check that the pH's are in the range 1.2-1.8. Adjust if necessary using a drop or two of 7.6N NH_4OH or 6N H Cl.

Solid Samples

1. Weigh powdered ($\leq$ 100 mesh) samples up to 0.5 g into 100 ml polymethylpentene (PMP) beakers.

2. Add 1 ml thorium-234 tracer solution.

3. Add 5 ml each of 8 N HNO_3, 6 N HCl and 14 N HF.

4. Cover beakers with close fitting plastic watch-glasses (do not use Speedy-Vap ribbed cover) and place on hotplate with surface temperature about 125°C for 1-2 hours.

5. Remove beaker covers but leave beakers on the hotplate. Add 25 ml 5% boric acid to each sample. Leave beakers uncovered on hot-plate for 1 hour further.

6. Set up Millipore vacuum filtration manifold with glass-fibre filter discs and 50 ml polycarbonate centrifuge tube receivers in place as appropriate. Place glass-wool plugs over the exposed filter surface to hold back the precipitate to come. Close with neoprene stoppers any manifold ports which are not to be used. It is convenient to use the manifold extension barrels for this filtration.

7. Pass the sample solutions through the filters and wash the PMP beakers and filters each with 5 ml water. Note that each filtrate and wash combined should not exceed 40 ml.

8. Add 1 ml lanthanum carrier solution (5 mg La) to each centrifuge tube and mix thoroughly using a plastic stir-stick.

9. Add 3 ml 14 N HF and again stir. Remove the stir stick.

10. Place tubes on water-bath at about 80°C for at least 1 hour or leave overnight at room temperature.

11. Spin tubes at 1500 rpm for 5 minutes then decant supernatant solution to waste.

12. Wash precipitate with 10 ml water. Repeat the centrifugation step and decant the wash solution to waste.

13. Add 5 ml 10% $Al(NO_3)_3$ pH 1.5 solution to the precipitate in the tube. Stir the tube contents using a polyethylene pasteur pipet and place the tube on a water bath at about 80°C for at least 15 minutes to effect dissolution of the precipitate.

14. Add 5 ml concentrated HNO_3, mix the solution and pass over an anion exchange column conditioned in 8 N HNO_3. The column: AG1-X8 100-200 mesh (originally chloride form) 0.7 x 5 cm.

15. Wash the column with 3 x 10 ml 8 N HNO_3. The first of these washes should be applied with a pasteur pipet to the walls of the funnel and column to ensure decontamination from lanthanum.

16. Elute the thorium with 10 ml 3% H_2SO_4 into a 10 ml volumetric flask.

17. Gamma-count the solutions in the volumetric flasks to determine chemical yield. Integrate the spectra between 60 and 95 keV. Subtract background similarly counted and integrated. Compare sample solution counts with 1 ml tracer solution taken directly as a comparator and made up to 10 ml in a volumetric flask.

18. Store the solutions in plastic bottles pending the autoanalyzer finishing process.

APPENDIX C

STEPWISE PROCEDURES FOR TRACER PREPARATION

Anion-exchange Column Preparation

1. Dissolve 35 g UO_3 or U_3O_8 in 1.2 L 9 N HCl. Filter the solution through a glass wool plug to remove insoluble material. Store the solution in a narrow necked vessel.

2. Prepare approximately 250 ml anion exchange resin bed in 9 N HCl in 2.5 x 50 cm column. Resin: AG1-X8 100-200 mesh, Cl^- form (Bio-Rad); Column: Econo-column 2.5 x 50 cm (Bio-Rad) plus funnel (Bio-Rad).

3. Place a glass-wool plug on top of the resin bed. Remove the funnel and install the column cap with luer fitting. Stop column flow with blank luer bottom fitting. Always leave a head of solution above the glass wool plug.

4. Attach thin tygon or equivalent plastic tubing to the cap luer fitting. Insert the free end of this tubing into the uranium solution container. Remove the bottom luer blank fitting and allow the column solution to flow into a narrow neck container of at least 1.5 L volume. The uranium solution will be syphoned through the column.

5. After the bulk of the uranium solution has passed through the column, remove the column cap with tube attached and wash out with water. Allow the uranium loading solution level to reach the resin surface, then wash the column walls above the resin surface with 2 x 10 ml 9 N HCl. Replace the blank luer bottom fitting to stop the flow and leave approximately 10 ml 9 N HCl head solution on the column.

6. When convenient, elute the column by syphon action (as above) with 1 L 9 N HCl to free the column from thorium. Leave column with approximately 10 ml 9 N HCl head solution and close both ends. The column is now ready for tracer production after a suitable period has elapsed for build-up of thorium-234.

Note that the column eluents and effluents are radioactive and give off HCl fumes. They should be appropriately handled, preferably in a fume-hood.

Tracer Elution

1. Elute the column with 150 ml 9 N HCl, preferably by syphon action to avoid HCl fumes. Collect the eluate in a partially covered 600 ml glass beaker.

2. Evaporate the solution to approximately 10 ml volume in a fumehood and then add about an equal volume of 9 N HCl.

3. Pass the solution over a 0.7 x 5 cm column of AG1-X8 100-200 mesh, Cl^- form resin conditioned in 9 N HCl. Collect effluent in 100 ml glass beaker.

4. Evaporate the column effluent solution to dryness. Dissolve the residue in 10 ml 8 N HNO_3 and pass over an identical column as in 3. above but conditioned in 8 N HNO_3. Then wash the column with 2 x 5 ml 8 N HNO_3.

5. Elute the thorium tracer with 20 ml 1 N HCl and dilute with water to the desired volume. Store in a screw cap polyethylene bottle.

The yield of this process is about 70% of the thorium present on the generator column.

APPENDIX D

STEPWISE PROCEDURES FOR AUTOANALYZER PROCESSES

Analysis of Water and Aerosol Sample Solutions

1. Using the flow diagram Figure 1, Section B as reference, check that all tubing and components on the autoanalyzer are in place.

2. Prepare reagents and standards as required from the flow diagram. (Note that the standard solutions for water and aerosol samples are not the same.)

3. Prime the system for 20 minutes by pumping water through all reagent and sample lines except line for TTA in kerosene. Pump kerosene through this line. Check bubble pattern, phase mixing in coils and phase separation at phase separators. Minor changes will be seen when system is switched to reagents. Check that there are no leaks. Turn on colorimeter.

4. Switch lines over to reagents. The amounts indicated in Appendix E should be sufficient for a typical 2 hour run. Using a plastic pipet, replace the water in the sample wash reservoir with 2 N HNO_3. Pump for 15 minutes.

5. Check bubble pattern, phase mixing in coils and phase separation. The air bubbles should be evenly spaced and effectively sweeping the reagents through the system. There should be good interaction of the organic and aqueous phases in the mixing coils to optimize extraction. In the first and second phase separators, there should be no aqueous solution in the diverted organic phase and only a small loss of organic phase to the aqueous phase. At the final phase separation, there must be no organic phase going into the aqueous fraction. Check that there are no air bubbles in the cell pull through line.

6. Turn on recorder and adjust optics to achieve baseline at zero deflection on chart recorder (see Technicon Manual).

7. Place 2-3 ml each of standard and saple solutions in sample tray as follows: duplicate calibration standards of 1.0 ug ml^{-1} thorium, duplicate standards of 0.1, 0.2, 0.5 and 1.0 ug ml^{-1} thorium, samples, final calibration standard of 1.0 ug ml^{-1} thorium.

8. After baseline has been steady for 10 minutes, start sampler. First peak will appear in 6-8 minutes. Adjust standard calibration potentiometer so that the response is 100% full scale for the first two calibration standards. Check that good hydraulics are maintained throughout run.

9. Turn off sampler after the last sample and standards have been aspirated.

10. After last peak has appeared, wash out analyzer for at least 10 minutes with water in all reagent lines before turning off pump.

11. Prepare a calibration curve by plotting percent chart deflection vs ug ml^{-1} of thorium in standards. Amount of thorium in the original sample in micrograms is ten times concentration found in ug ml^{-1} corrected for chemical yield using thorium tracer.

Analysis of Solid Samples

1. Set up the autoanalyzer for "straight" chemistry using flow diagram Figure 2, Section B as reference.

2. Prepare reagents and standards as required from the flow diagram. (Note that the standards for solid samples are not the same as those used for water and aerosol samples.)

3. Prime system by pumping with water for at least 10 minutes. Check for leaks and good bubble pattern. Turn on colorimeter.

4. Switch over to reagents. Replace water in wash reservoir with 1 M nitric/sulphuric acid solution. Pump for 10 minutes or more.

5. Check bubble pattern in mixing coil and that the cell pull through line is free of bubbles.

6. Turn on recorder and adjust optics to achieve baseline at zero deflection on chart recorder (see Technicon manual).

7. Place 1-2 ml each of standards and samples solutions in sample tray as follows: duplicate calibration standards of 1.0 ug ml^{-1} thorium, duplicate standards of 0.1, 0.2, 0.5 and 1.0 ug ml^{-1}, samples, final calibration standard of 1.0 ug ml^{-1}.

8. After baseline has been steady for 10 minutes start sampler. First peak will appear in 5-6 minutes. Adjust standard calibration potentiometer so that response is 100% full scale for the first two calibration standards.

9. Turn off sampler after all standards and samples have been aspirated.

10. After last peak has appeared, wash out analyzer for at least 10 minutes by pumping water in reagent lines before turning off pump.

11. Prepare a calibration curve by plotting percent chart deflection vs ug ml^{-1} of thorium in standards. Amount of thorium in the original sample in micrograms is ten times concentration in ug ml^{-1} corrected for chemical yield using thorium tracer.

PREPARATION OF REAGENT SOLUTIONS

1. Iron carrier, 5 mg/ml Fe
   Dissolve 4.3 g $FeNH_4(SO_4)_2 \cdot 12H_2O$ in 100 ml deionized water.

2. Lanthanum carrier, 5 mg/ml La
   Dissolve 1.6 g $La(NO_3)_3 \cdot 6H_2O$ in 100 ml deionized water.

3. Hydroxylamine hydrochloride 5%, pH 1
   Dissolve 50 g $NH_2OH.HCl$ in 1L deionized water. Adjust to pH 1.0 with dilute hydrochloric acid and/or ammonium hydroxide.

4. Hydroxylamine hydrochloride 5%, 0.5 mg/ml Fe, pH 1.5
   Dissolve 4.3 g $FeNH_4(SO_4)_2 \cdot 12H_2O$ in 1L solution 3 above. Adjust to pH 1.5 with dilute hydrochloric acid and/or ammonium hydroxide.

5. Ammonium hydroxide 7.5 N
   Dilute reagent grade concentrated ammonium hydroxide solution 1:1 with water.

6. Hydrofluoric acid 14N
   Dilute reagent grade concentrated hydrofluoric acid 1:1 with water.

7. Hydrochloric acid 6N
   Dilute reagent grade concentrated hydrochloric acid 1:1 with water.

8. Nitric acid 8 N
   Dilute reagent grade concentrated nitric acid 1:1 with water.

9. Boric acid 5%
   Dissolve reagent grade H_3BO_3 in water, e.g. 50 g in 1 L.

10. Sulphuric acid 3%
    Add 30 ml reagent grade concentrated sulphuric acid to 970 ml water.

11. Nitric/Sulphuric acid (approximately 1 N in both) Dilute 100 ml solution 8 to 1 L with solution 10.

12. Aluminum nitrate 10%, pH 1.5
    Dissolve reagent grade $Al(NO_3)_3 \cdot 9H_2O$ in water, e.g. 100 g in 1 L. Adjust to pH 1.5 using dilute nitric acid and/or ammonium hydroxide.

13. Thenoyltrifluoroacetone (TTA) 0.08 M
    Dissolve 5.3 g TTA in 300 ml kerosene. (May require slight warming to completely dissolve.) This amount is sufficient for a 2 hour run.

14. Ammonium acetate wash solution, pH 1.5
Prepare a saturated stock solution of CH_3COONH_4 in water. Dilute 20 ml of this to 1L with water and adjust to pH 1.5 with dilute nitric acid and/or ammonium hydroxide.

15. Arsenazo-III 0.01% in 2 N nitric acid
Dissolve 0.030 g Arsenazo-III in 300 ml 2 N HNO_3 by stirring vigorously, no warming. Filter the solution through a Whatman 40 paper. This amount is sufficient for a 2 hour run. Make up fresh for each run.

16. Arsenazo-III 0.02% in water
Dissolve 0.020 g Arsenazo-III in 100 ml deionized water. Filter the solution through a Whatman 40 paper. This amount is sufficient for a 2 hour run.

17. Thorium standards for water samples
Dilute atomic absorption standard 1000 ppm thorium solution with hydroxylamine hydrochloride (solution 4. above) to appropriate concentrations in the range 0.0-1.0 ug ml^{-1} thorium.

18. Thorium standards for aerosol samples
Add 500 ml water and 0.6 ml 14 N HF (solution 6. above) to 50 g $Al(NO_3)_3.9H_2O$ in a 1L beaker and stir to dissolve. Add 100 ml lanthanum carrier (solution 2. above) and make volume to 1L. Adjust to pH 1.5 with dilute nitric acid and/or ammonium hydroxide. Use to dilute atomic absorption standard 1000 ppm thorium solution to appropriate concentrations in the range 0.1-1.0 ug ml^{-1} thorium.

19. Thorium standards for solid samples
Use solution 11 above to dilute atomic absorption standard 1000 ppm thorium solution to appropriate concentration in the range 0.0 - 1.0 ug ml^{-1} thorium.

USE ONLY ANALYTICAL REAGENT GRADE CHEMICALS

APPENDIX F

COLORIMETRIC DETERMINATION OF TOTAL THORIUM[2]
(Method currently in use at AECB, Ottawa)

THE COLORIMETRIC DETERMINATION OF TOTAL THORIUM

PRINCIPLE

Two of the most sensitive methods for the detection of thorium-232 are chemical methods, the fluorimetric determination with morin[1] and the colorimetric determination with arsenazo III[2]. Due to the low specific activity of thorium-232 (0.109 pCi/ug) these photometric methods are capable of detecting lower levels of this radionuclide than can be detected by alpha-counting methods. Of the foregoing methods, the colorimetric determination with arsenazo III has been selected. Because arsenazo III is not specific for thorium but reacts with many quadrivalent ions, it is necessary to chemically isolate thorium before applying the colorimetric development. Thorium is isolated from prepared sample solutions by coprecipitation first with lanthanum hydroxide then with lanthanum fluoride followed by extraction with thenoyltrifluoroacetone (TTA) in a suitable solvent. The organic extract is stripped with a nitric acid solution to produce an aqueous solution of thorium. The colour development is performed by reacting a strong HCl solution (approx 6M) of the isolated thorium with an aqueous solution of arsenazo III. The colorimetric measurement is then performed at a wavelength of 665 nm.

APPLICATION

This method may be applied to all types of water, biological, ore and soil samples following their transformation to appropriate aqueous solutions. The lanthanum fluoride coprecipitation and TTA extraction of thorium provides adequate isolation for most samples. There are some cases where extra chemical separations will be required. One of these is the analysis of bone ash. Due to high levels of calcium and phosphate in this material, a very heavy precipitate of calcium phosphate will form when the precipitation of lanthanum (thorium) hydroxide is attempted. Consequently it is necessary to make a separation of lanthanum and calcium oxalates from the phosphate. After calcining the oxalate and redissolving the oxides, lanthanum may be separated from the calcium by precipitating lanthanum (thorium) hydroxide at a pH of 9. The hydroxides are dissolved and lanthanum (thorium) fluoride may now be precipitated without the interference of calcium. Other samples which are high in aluminum or calcium plus phosphate will normally require the extra oxalate separation.

Although the fluorometric morin method is about 5 times more sensitive than the arsenazo III method, it has certain requirements which make it not as suitable for routine application. Because it is a fluorometric method it is very susceptible to interference from trace impurities in reagents and is quite sensitive to temperature fluctuations in the sample solution during the measurement of fluorescence. In addition, it requires a fluorimeter with a tungsten light source. Not all filter-type fluorimeters have provision for tungsten lamp excitation. The arsenazo III method can be performed with commonly available spectrophotometers and will provide sensitivity adequate for most purposes.

The detection limit for the arsenazo III spectrophotometric method is approximately 0.05 ug of thorium. For thorium-232 this corresponds to 0.0055 pCi. This is a much smaller activity than can be detected by alpha spectrometry. For thorium-228 and thorium-230 the most sensitive method is alpha spectrometry because of the much higher specific activity of these isotopes.

APPARATUS

1. Spectrophotometer capable of accommodating 4- or 5-cm light-path cells.
2. Spectrophotometer cells; 4- or 5-cm path length.

[1] Sill, C.W., and Willis, C.P. Anal. Chem; 36: 622; 1964.

[2] Bazzano, E., and Gersini, G. Anal. Chim. Acta; 38: 460; 1967.

3. Separatory funnels; 125-ml, with Teflon stopcock.
4. Magnetic stirrer.
5. Teflon-coated magnetic stir-bars; 10 x 3 mm and 1 x 3/8 inch.
6. Plastic centrifuge tubes, 50-ml.
7. Platinum crucibles, 30-ml.
8. Vycor crucibles, 45-ml.

REAGENTS

1. 0.25M TTA (Thenoyltrifluoroacetone) – dissolve 27.8 g of TTA in benzene and dilute to 500 ml.
2. Arsenazo III solution – dissolve 0.4 g of arsenazo III in water and dilute to 1 litre. Store in the dark.
3. Lanthanum carrier solution – dissolve 11.728 g of La_2O_3 in 15 ml of concentrated HNO_3 and dilute to one litre. This solution contains 10 mg La per ml.
4. Fluoride wash solution – dilute 60 ml of HNO_3 and 30 ml of HF to one litre with deionized water. Store in a plastic bottle.
5. Oxalic acid solution – dissolve 100 g of oxalic acid in water and dilute to 1 litre.
6. Oxalic acid wash solution – dilute 100 ml of the oxalic acid solution to 1 litre.
7. 5% $NaHSO_4$ – dissolve 5 g of $NaHSO_4.H_2O$ in water and dilute to 100 ml. Filter before using.
8. 2M HNO_3 – dilute 130 ml HNO_3 to 1 litre with deionized water.
9. 2M $Al(NO_3)_3$ solution – dissolve 750 g of $Al(NO_3)_3.9H_2O$ in water and dilute to 1 litre.
10. Saturated ammonium acetate – add an excess of solid ammonium acetate to deionized water.
11. pH 1.5 wash solution – add 20 ml of saturated ammonium acetate to 1 litre of deionized water and adjust the pH to 1.5 with HNO_3 and NH_4OH.

SAMPLE PREPARATION

WATER SAMPLES – Samples should be acidified to 1% HNO_3 in the field when they are collected. For dissolved thorium only, the sample is filtered through a 3.0-μ membrane filter before acidification. To 1010 ml of sample add 5 ml of perchloric acid, 2 ml of lanthanum carrier and evaporate to perchloric fumes to destroy all organic matter. Repeat with the addition of 10 ml of nitric acid if necessary. Add 5 ml HNO_3 and transfer to a 100-ml centrifuge tube. Dilute to about 75 ml and proceed to the DETERMINATION.

BIOLOGICAL SAMPLES – All samples may be dry ashed. See procedure Ra-01 for ashing conditions. For flesh and vegetation ash dissolve 1 g of ash plus 2 ml of lanthanum carrier in 1:1 HNO_3 and dilute to about 100 ml. Proceed to DETERMINATION. If large amounts of silica are present in the ash it should be treated with HNO_3 and $HClO_4$ and then heated to fumes of $HClO_4$ in order to dehydrate the silicates. Redissolve in 5 ml HNO_3, dilute to 30 ml and centrifuge, discarding the silica precipitate. Return the supernate to the centrifuge tube and proceed to the DETERMINATION.

For bone samples it is necessary to perform the oxalate separation. Dissolve 1 g of bone ash plus 2 ml of lanthanum carrier solution in 1:1 HNO_3 and bring the final volume to about 100 ml with water. Adjust the pH to 4 with 20% NaOH and heat to near boiling. While stirring add 4 ml of oxalic acid solution. Digest the precipitate for an additional 5-10 min then cool and centrifuge. Discard the supernate. Wash the precipitate with 30 ml of oxalic acid wash solution, centrifuge and discard the supernate. Dissolve the precipitate in 5 ml HNO_3 and add 0.5 g $KClO_3$. Heat very cautiously to decompose the oxalate and continue until gas evolution ceases. Dilute to approximately 75 ml in a 100-ml centrifuge tube and proceed to the DETERMINATION.

SOIL, ORE AND ROCK SAMPLES – Weigh a dried, 1-g sample into a platinum crucible, add 2 ml of lanthanum carrier and ash all organic matter by heating over a burner or by heating overnight at 550°C in a muffle furnace. To the cooled, ashed sample add 3 ml H_2SO_4 plus 10-20 ml HF. Heat on a hot plate in a fume hood to drive off the silicon tetrafluoride and the excess HF. If necessary, repeat with the addition of HF to remove all silica. Heat to strong SO_3 fumes and cool. Add 3 to 5 g of potassium pyrosulphate (depending on the amount of residue) and begin heating over a gas burner. Continue heating and

swirling until a clear melt is obtained. Cool and dissolve in 100 ml of 10% HCl (use a 200-250 ml beaker). Proceed to DETERMINATION.

DETERMINATION

1. To the 75 ml of sample solution in the centrifuge tube or 100 ml of soil or ore digest in a beaker, add NaOH to pH 9. Digest the precipitate for 30 minutes in a hot water bath, cool and centrifuge. Discard the supernatant liquid.
2. Redissolve the hydroxide precipitate in 5 ml HCl. Heat if necessary. Dilute to 75 ml (100 ml for soil or ore samples) and repeat the precipitation with NaOH (pH 9). Digest, cool and centrifuge. Discard the supernate.
3. Redissolve the hydroxides in 4 ml HNO_3. If the precipitate is hard to dissolve, the addition of 5-10 drops of 30% hydrogen peroxide may facilitate the process.
4. Transfer the dissolved lanthanum hydroxide solution to a transparent plastic centrifuge tube with washing and dilute to 30 ml.
5. Add 5 ml of 48% HF and stir at room temperature for 1 hour. Centrifuge and discard the supernate.
6. Wash the lanthanum fluoride precipitate with 10 ml of the fluoride wash solution. Centrifuge and discard the wash solution.
7. Add 5 ml of 2M $Al(NO_3)_3$ and 2 ml HNO_3 to dissolve the lanthanum fluoride precipitate. Add 1 ml of saturated ammonium acetate and dilute to 30 ml. Adjust the pH to 1.5 using NH_4OH.
8. Transfer the solution to a 125-ml separatory funnel with washes of pH 1.5 wash solution.
9. Add 20 ml of 0.25M TTA-benzene extractant and shake for 5 minutes. Allow the phases to separate and transfer the aqueous phase to a clean 125-ml separatory funnel.
10. Add a second 20-ml volume of extractant to the aqueous phase and shake for 5 min. Allow the phases to separate and discard the aqueous phase. Transfer the second organic extract to the separatory funnel containing the first extract.
11. Wash the combined organic extracts with 25 ml of the pH 1.5 wash solution. Allow the phases to separate and discard the wash solution.
12. Add 20 ml of 2M HNO_3 to the washed organic extracts and shake for 5 minutes. After the phases have separated, drain the nitric acid solution into a 50-ml beaker.
13. Repeat the 2M HNO_3 strip with an additional 20 ml and combine with the first strip.
14. Add 2 ml of $HClO_4$ and 2 ml of 5% $NaHSO_3$ to the combined strip solutions and evaporate to fumes of $HClO_4$. Continue heating on hot plate with a surface temperature of 200°C to incipient dryness. Do not bake the residue or insoluble thorium salts may be formed.
15. Dissolve the residue in a few mls of 1:1 HCl and transfer to a 10-ml volumetric flask containing 1 ml of Arsenazo III solution. Wash the beaker with small amounts of 1:1 HCl and continue adding these to the volumetric flask until the 10-ml volume is reached.
16. Measure the absorbance of this solution at 665 nm using 4-cm cells. Use 1 ml of Arsenazo III solution diluted to 10 ml with 1:1 HCl as the reference blank.
17. Carry a set of thorium standards (0.1 to 5 ug Th) through the entire procedure for calibration purposes.

CALCULATIONS

Prepare a calibration curve by plotting absorbance (665 nm) vs amount of Th (ug). This calibration curve will correct for recovery throughout the entire procedure. The amount of thorium contained in the original sample aliquot can be read directly from the calibration curve.

PRECISION AND DETECTION LIMIT

The relative standard deviation for thorium standards carried through the procedure is approximately ±3% of the amount present above 0.5 ug Th. The detection limit when using 4-cm cells is 0.05 ug Th. For a 500-ml water sample this corresponds to a detection limit of 0.1 ug/litre.

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